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TAMPA BAY AREA
PHOTOCHEMICAL OXIDANT STUDY

DATE JAN 1978
FINAL REPORT
APPENDIX C

EMISSION RATE FOR BIOGENIC NO_x

U. S. ENVIRONMENTAL PROTECTION AGENCY
REGION IV
AIR & HAZARDOUS MATERIALS DIVISION
ATLANTA, GEORGIA 30308

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EMISSION RATES FOR BIOGENIC NO_x

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ABSTRACT

A literature review of biogenic sources of NO_x was conducted to determine their emission rates into the atmosphere. NO_x are some of the products of microbial denitrification, chemical decomposition of nitrites and the oxidation of organic nitrogen compounds. There appears to be no significant emission of NO_x from either oceans or freshwaters. Biogenic emission rates for NO and NO_2 from soil range from 0.015 to 0.02 kg NO km^{-2} hr^{-1} and 0.01 to 0.2 kg NO_2 km^{-2} hr^{-1}. Submerged soils, sediments, marshes and swamps could be sources of NO_x but emission data are not available. There is no significant evidence of NO_x emission from living vegetation. During decay, decomposition and ensiling of vegetation, NO_x can be formed. Although the emission rates are not known, they are probably not significant.

The estimates of NO_x emission rates from the above biogenic (soil) sources were computed for a global basis and then compared closely to previously estimated natural global emissions. Also, the background atmospheric concentrations of NO_x are similar to those levels predicted from biogenic emission rates.

INTRODUCTION

Several authors have estimated global biogenic NO_x emissions. Robinson and Robbins (1970) estimated global natural emissions of NO_x at 768×10^9 kg NO_2 which was approximately 15 times the anthropogenic emissions (53×10^9 kg NO_2). McConnell (1973) suggested that the natural sources of NO_x were 4 times the anthropogenic sources. Galbally (1975) estimated biogenic NO_x emissions for the northern hemisphere at 1×10^9 kg NO_2 yr^{-1} and the anthropogenic emissions at 0.5×10^9 kg NO_2 yr^{-1}. Estimates of biogenic emissions for NO_x for Ohio and surrounding states, ranged from 1.7 to 4.1×10^8 kg NO_2 yr^{-1} and the anthropogenic emissions ranged from 2.5 to 33.3×10^8 kg NO_2 yr^{-1} (RTI, 1974). These calculated NO_x emissions were based on atmospheric concentrations and a theoretical balance of nitrogen compounds. At present there is no general agreement on the relative contributions of the biogenic and anthropogenic emissions. Most biogenic emission rates were derived from the amounts of NO_x needed to balance nitrogen cycles or were deduced theoretically.

The objectives of this literature review were to gather information on possible biogenic sources of NO_x, to determine biogenic emission rates and to discuss the factors affecting NO_x emissions. The nitrogen cycle is discussed to suggest possible biogenic sources of nitrogen oxides. The biogenic sources and emission rates of NO_x are divided into the following categories: 1) water: ocean and freshwaters; 2) soil; 3) flooded soil, sediments, swamp and marsh; and 4) vegetation. The biogenic emission rates determined from the

literature were compared to other emission estimates and atmospheric concentrations.

NITROGEN CYCLE

Nitrogen is found in five major sinks in the biosphere: primary rocks, sedimentary rocks, the deep-sea sediment, the atmosphere, and the soil-water pool. Approximately 98% of the earth's nitrogen is in primary and sedimentary rocks, while the atmosphere contains about 2%; the deep-sea sediment and soil-water pool together contain less than a percent of the global nitrogen (Burns and Hardy, 1975).

In the atmosphere, N_2 is the major nitrogen constituent while nitrogen oxides (N_2O, NO, NO_2), NO_3^-, NO_2^-, NH_3, and NH_4^+ are present in the ppm range or less. The soil-water pool can contain a large amount of dissolved N_2. N_2O, NO, and NO_2 can also occur in soils for short time periods under specific environmental conditions.

A simplified nitrogen cycle showing nitrogen transformations in the soil-water pool and transfers between the soil-water pool and the atmosphere is shown in Figure 1. Nitrogen enters the soil-water pool through biological nitrogen fixation, industrial fixation, precipitation and application of fertilizers. Biological fixation reactions occur either in free-living organisms (i.e. Azotobacter) or in symbiotic plant-microbial associations (i.e. Rhizobium). Plants and microorganisms utilize NH_4^+, NO_3^-, and NO_2^- from the soil-water pool and nitrogen undergoes a multitude of chemical and biological transformations.

In nitrification (Figure 1), an aerobic process, ammonium is oxidized to nitrate.

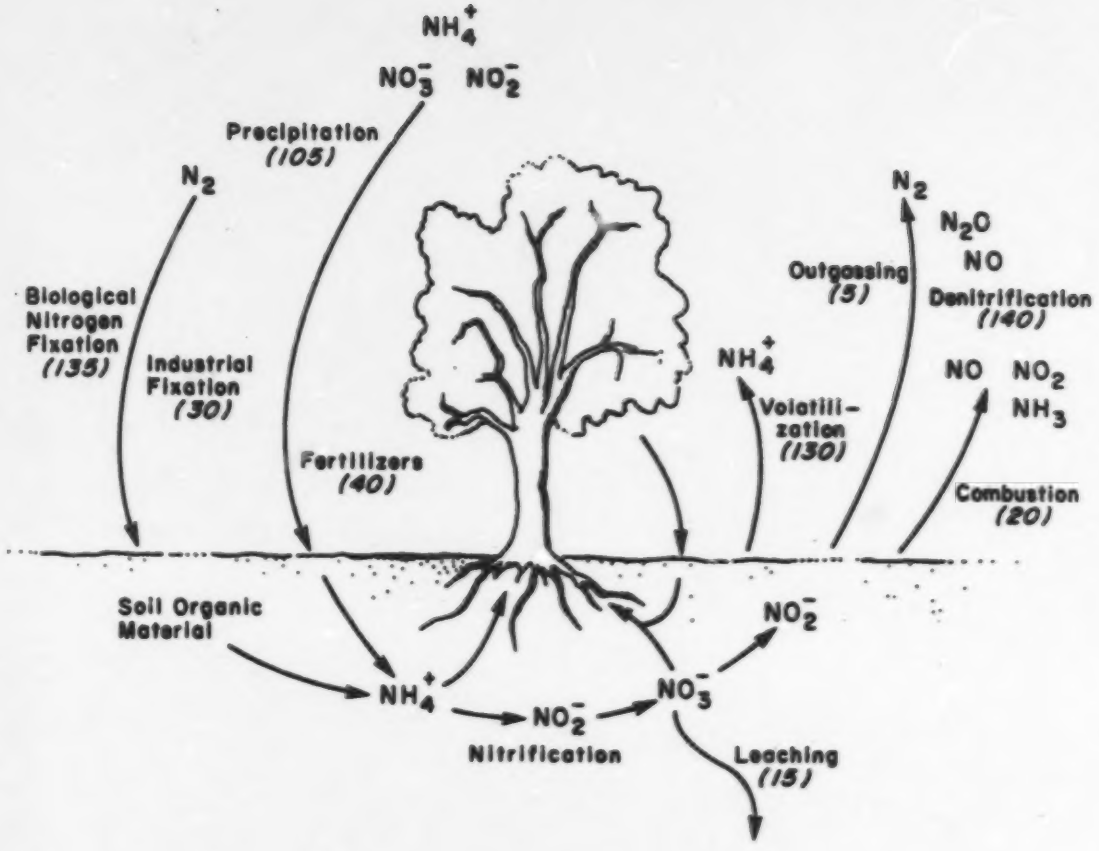

Fig 1. Terrestrial nitrogen cycle showing nitrogen transfer and transformations. Values given are metric tons (N) × 10^6 yr^{-1} (Burns and Hardy, 1975; Hardy and Havelka, 1975).

$$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$$

Oxidation occurs mainly by the autotrophic bacteria of the Nitrobacteriacea. The genus Nitrosomonas oxidizes ammonium to nitrite and the genus Nitrobacter oxidizes nitrite to nitrate. Other microorganisms, including certain bacteria, molds and fungi, are capable of limited oxidation of nitrogen, but their contribution to nitrification is limited. The rapid nitrification of ammonium is important agriculturally, since fertilizer ammonium can be rapidly oxidized to nitrate and then lost from the soil by denitrification, leaching and chemical decomposition (Hauck, 1971).

In denitrification (Figure 1), an anaerobic metabolic process, nitrate is reduced sequentially to NO, N_2O or N_2.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O, N_2$$

The reduction is carried out by a diverse group of bacteria but the non spore formers such as Pseudomonoas, Micrococcus, and Achromobacter and spore-forming species of Bacillus are the principal denitrifiers.

BIOGENIC SOURCES OF NITROGEN OXIDES

WATER

Oceans

The nitrogen cycle in the oceans is complex in respect to the large geographical translocations of nitrogen and in species composition of micro- and macro-organisms (Dudgale, 1969). Theoretical models of nitrogen circulation in oceans and mass balances for marine nitrogen cycles indicate that inorganic nitrogen is removed or lost from the oceans (Yoshinari, 1976; Dugdale, 1969). Denitrification is a significant factor in loss of nitrogen from the marine environment, especially in oxygen-deficient waters. Goering

and Cline (1970) determined that denitrification in raw seawater occurred in two stages. First, nitrate was reduced to nitrite, and second, the nitrite was further reduced, presumably to N_2. Nitrate^{15}-N added to water samples from the oxygen-deficient layer in the tropical Pacific resulted in the production of nitrite and N_2. Denitrification rates varied from 7-150 µg N/l/day depending on sample depth (Goering, 1968). Estimated denitrification losses in oxygen-deficient waters of the Black Sea (7×10^9 - 2×10^{11} g N yr^{-1}) and Cariaco Trench (1×10^{10} g N yr^{-1}) were not significant compared to those in the eastern tropical North Pacific (1×10^{13} g N yr^{-1}) (Goering et al., 1973).

Patriquin and Knowles (1974) examined shallow-water marine sediments from several locations for denitrifiers and found that most of the bacteria that reduced nitrate to nitrite also reduced nitrite to gaseous nitrogen. Bacterial isolates varied considerably in the rate of N_2 production and N_2O reduction, and in accumulation of N_2O. Barbaree and Payne (1967) demonstrated that N_2O and very small quantities of NO were present transiently in the atmosphere over reaction mixtures containing cell-free extracts of Pseudomonas perfectomarinus cells.

The above data support the conclusion that denitrification is an active process in the oceans and that both N_2 and N_2O are products but there is no evidence of NO_x production in oceans.

Freshwater

As in the oceans, denitrification in freshwaters is a significant factor in nitrogen loss. The nitrogen cycle and the fate of nitrogen in freshwaters has been reviewed recently (Keeney, 1973; Brezonik, 1973).

In lakes, denitrification occurs mainly in the oxygen depleted hypolimnic layers where inorganic nitrogen levels are at a minimum (Vollenweider, 1968). Denitrification rates in Smith Lake, Alaska, in water one meter below the ice were measured at 15 µg N/liter/day. Molecular nitrogen appeared to be the only significant product and NO and N_2O were not detected (Goering and Dugdale, 1966). Brezonik (1973) concluded that denitrification did not appear to be significant in Florida lakes. Of the 55 north central lakes sampled in Florida, only four developed anoxic conditions at the bottom and the nitrate concentrations in Florida lakes are typically low. Nitrogen is the only product of denitrification released in significant quantity, and seldom is NO or N_2O detected (Payne, 1973).

In addition to denitrification, there is the possibility of chemical decomposition of nitrite to produce gaseous nitrogen products. In some lakes, concentrations of polyphenolic substances (tannins, lignins, humic acid) are high and pH of water is acidic. Under these conditions the reaction of nitrous acid with organics could be important as a source of nitrogen oxides (Brezonik, 1973).

SOIL

The soil is an open system from which various nitrogen forms volatilize into the atmosphere. As early as 1944, it was discovered that nitrous oxide was one of the constituents of soil air (Kriegel, 1944). Adel (1946, 1951) suggested that N_2O was produced in the soil and was the source of atmospheric N_2O. Arnold (1954) confirmed N_2O losses from the soil and Wijler and Delwiche (1954) found that N_2O was the major initial product of denitrification under some soil conditions, but also identified NO as an additional product. More

recently, in addition to losses from denitrification, investigators have found that NO and NO_2 are produced by chemical reactions in soil involving HNO_2 and nitrite. (Reuss and Smith, 1965; Nelson and Bremner, 1970; Bollag, et al., 1973).

Denitrification

The term "denitrification" implies the gaseous loss of nitrogen to the atmosphere, usually as N_2, N_2O or NO, through some biological agency and it is the subject of two recent reviews (Payne, 1973; Delwiche and Bryan, 1976). In the absence of oxygen, microorganisms use nitrate or its reduction products as electron acceptors for the oxidation of some organic compound as an energy-yielding reaction. The intermediates and products of denitrification have been studied in cultures and in soil experiments, but the pathways are varied and not presently elucidated. One possible pathway is as follows:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N$$

Many genera of bacteria are able to reduce nitrate to nitrite and of those a limited number are able to further reduce nitrite to N_2O or N_2. Studies have determined that NO is a specific product of nitrite reduction; nitrous oxide (N_2O) results from NO reduction and is the terminal denitrification product of several bacterial strains (Renner and Becker, 1970; Payne, Riley and Cox, 1971).

Factors Affecting Denitrification. Denitrification is influenced by factors such as soil oxygen concentration, redox potential, pH, soil organic matter content and temperature. In general, conditions that directly or indirectly decrease the soil oxygen content or increase microbial activity increase denitrification. When soil oxygen level decreased from 8.5% to 1%,

N_2O production increased, but as the oxygen level decreased to zero the N_2O was reduced to N_2 (Cady and Bartholomew, 1961). Although it was not measured, a similar response would be expected for NO. In a closed soil-plant system (Stefanson, 1972) N_2 was the major component of denitrification but in the absence of plants the main product was N_2O. Over the temperature range of 15 to 35°C, increasing the temperature 10°C doubled the rate of denitrification (Stanford et al., 1975). Bailey (1976) reported that as soil temperature increased the rate of N_2 production increased and NO production decreased. Denitrification capacities of 17 surface soils were significantly correlated with total organic carbon content and very highly correlated with water-soluble organic carbon or mineralizable carbon (Burford and Bremner, 1975). Nitric oxide was detected in the atmosphere of several soils incubated at 20°C for 7 days, but the amount represented not more than 0.1% of the nitrate lost. As the soil pH increased from 5 to above 7, the ratio of N_2O to N_2 decreased (Burford and Bremner, 1975); below pH 7.0, N_2O was the main product (Wijler and Delwiche, 1954). The pH dependency of NO production should be similar to N_2O. In general, low temperature, low pH, and marginal anaerobic conditions favor the production of N_2O relative to N_2 (CAST, 1976).

Chemodenitrification or Nonbiological Chemical Decomposition

In addition to microbial denitrification there is increasing evidence that non biological reactions produce nitrogen gas or nitrogen oxides under some circumstances (Delwiche and Bryan, 1976; Porter, 1971). Non biological loss of nitrogen may result from "side-tracking" during nitrification and denitrification processes. This can occur when an intermediate in the process (i.e. NO_2^-) is produced more rapidly than it can be oxidized or reduced bio-

logically and undergoes chemical decomposition (Lance, 1972). There are several non biological reactions that could release NO into the atmosphere.

Nitrosation denotes the addition of the nitroso group (-N = O) to an organic molecule, and is brought about by HNO_2 and other compounds to form an organic complex (O = N - X). The nitroso groups formed are labile and react further with the nitrosating agent to form gaseous products.

$$HNO_2 \rightarrow NO^- + OH$$

$$NO^- + R \rightarrow N = O - R$$

$$N + O - R + A \rightarrow NO + A - R$$

Stevenson, et al. (1970) showed evidence that NO, N_2O, and N_2 could be produced by nitrosation of humic and fulvic acids, lignins, and aromatic substances at pH 6.0 and 7.0 in the absence of oxygen. Steen and Stojanovic (1971) found that NO was volatilized from a calcareous soil when high concentrations of urea were nitrified with concurrent accumulation of nitrite and assumed that nitrosation between nitrous acid and organic matter was the main pathway by which NO was formed.

Wullstein and Gilmour (1964, 1966) reported that nitrite reacted with certain reduced transition metals in sterile, moderately acid systems to yield NO as a primary gaseous product. In their proposed scheme, NO_2^- and NO reacted with metallic ions to form complexes which were either stable or reactive. The metals could also react directly with NO_2^- or NO without forming complexes or intermediates to form NO or N_2. They concluded that copper and manganese ions in the soil were primarily responsible in reacting with nitrite. Nelson and Bremner (1970) found that Cu^+, Sn^{2+} and Fe^{2+} were the only metallic cations that promoted nitrite decomposition and that soils normally do not

contain sufficient amounts of these cations under conditions suitable for chemodenitrification to be significant in nitrite decomposition.

Reuss and Smith (1965) showed that N_2 and N_2O are formed by chemical decomposition of nitrite in soil and also showed that NO_2 was evolved when nitrite was added to acid soils. Bremner and Nelson (1968) found that N_2 and NO_2 and small amounts of N_2O were formed when nitrite was added to neutral and acid soils. They suggested that the reactions between soil organic constituents and nitrite were responsible for the formation of N_2 and N_2O, while self-decomposition of HNO_2 was responsible for the formation of NO and NO_2. In the steam-sterilized raw humus samples incubated with nitrite, NO was the predominant gaseous reaction product (Nommick and Thorin, 1971). Nelson and Bremner (1970) found that the formation of NO_2 by decomposition of nitrite in pH 5.0 solution was not promoted by organic and inorganic soil constituents, and concluded that most of the NO_2 evolved was formed by self-decomposition of HNO_2. The amount of NO_2 formed was inversely related to soil pH, but pH had little effect on the amount of nitrite converted to nitrate. These findings led to the conclusion that the self-decomposition reaction of HNO_2 was best represented by the equation:

$$2HNO_2 \rightarrow NO + NO_2 + H_2O$$

Measurements of NO and NO_2 emissions from soil and biological and non biological reactions are difficult and only limited data are available (Table 1). Soil emission rates were determined by directly trapping liberated gases at the soil surface. Based on the limited number of studies, NO is produced at lower rates (0.004 to 0.02 kg NO km^{-2} hr^{-1}) than NO_2 (0.01 to 0.2 kg NO_2 km^{-2} hr^{-1}). These rates are temperature dependent and would be expected to increase as the temperature increases (Bailey, 1976).

Table 1. Nitrogen Oxide Flux From Soil

Soil or Medium	N Addition	Type N Oxide	$kg/km^2/hr.$ Emission Rate	Reference
low humic Ordinary Chernozem	$NH_4 NO_3$ urea	NO	.015-.02	Getmanets, 1972
Chernozem Podzol	$NH_4 NO_3$ 100 Kg. N/ha	NO	.006 .004	Borisova, et al., 1972
top soil from pine, oak, sod stand (sandy loam)	none	NO_2	pine 0.125 oak 0.07 sod 0.11	Kim, 1973
Sod- Podzolic	$NH_4 NO_3$	NO_2	0.01-0.2 comment: variation during the growing season	Makarov, 1969
Sod - Podzolic medium clay loam	urea 240 Kg/ha	NO_2	0.03-0.05	Makarov and Ignatova, 1964
raw humus in spruce stand (feather moss)	KNO_3 $NH_4 NO_3$ $Ca (NO_3)_2$ $Al (NO_3)_3$	*$(NO+NO_2)$	.018 .029 .035 .104	Mahendrappa, 1974
raw humus (sphagnum moss)	$NH_4 NO_3$ $Ca (NO_3)_2$ $Al (NO_3)_3$	*$(NO+NO_2)$	.012 .018 .035	Mahendrappa, 1974

* emission rate calculated as NO_2

FLOODED SOIL, SEDIMENTS, SWAMP AND MARSH

Flooded soil or sediments have characteristics that are unique and separate them from arable soil, such as the interruption of gaseous exchange between air and soil (Patrick and Mikkelsen, 1971). The restriction of oxygen diffusion results in an oxidized layer of up to one cm. in the soil-water interface, but below this layer the oxygen content declines rapidly. A second characteristic of flooded soil is a change in microbial forms from aerobic to facultative anaerobic organisms to anaerobic bacteria. Retarded metabolic processes are reflected in reduced organic matter decomposition and a lowered nitrogen requirement for decomposition. In terms of physiochemical changes, the pH of flooded soils tends to change toward neutrality, redox potentials are low (-300 mv) and there is an increase in the amount of ions in the soil solution (Ponnamperuma, 1972).

In submerged soil, inorganic nitrogen is present almost exclusively as NH_4^+ because the lack of oxygen prevents the nitrification of NH_4^+ to NO_3^-. However, the NO_3^- formed in the aerobic layer at the sediment-water interface diffuses downward to the anaerobic layer where denitrification occurs. As in soils, denitrification (biological and non-biological) is the major source of nitrogen oxides from flooded soils, sediments, swamps and marshes. Oxygen content, pH, redox potential, temperature, nitrate content and organic matter content of submerged soils are factors that affect the amount and products of denitrification.

Denitrification as measured by nitrate and nitrite reduction rates and N_2 formation is significant in submerged soil and sediments (Chen, Keeney, Konrad, Holding, Graetz, 1972; Chen, Keeney, Graetz and Holding, 1972; Reddy and Patrick, 1975; Engler and Patrick, 1974; Goering and Dugdale, 1966). The

disappearance of nitrate in sediments and submerged soils is usually accompanied by the production of N_2 but recently several workers have shown other denitrification products. Lake sediments incubated with nitrate and nitrite produced N_2O in addition to N_2 (Macgregor and Keeney, 1973; Chen, Keeney, Konrad, Holding, Graetz, 1972). In the decomposition of nitrite in flooded soils, N_2 was produced at all pH's but NO and N_2O were produced only at pH 6.0 and below (Van Cleemput, et al. 1976). The addition of a soil sterilant ($HgCl_2$) increased the rate of NO production. The important conclusions from this study were that under acid conditions significant amounts of N_2, N_2O and NO were formed. The production of NO under acid conditions with and without a sterilant suggested the self-decomposition of nitrous acid similar to what occurs in arable soils. However, the data are not adequate to calculate emission factors.

VEGETATION

Plant leaves and roots can absorb both reduced or oxidized forms of nitrogen from the environment and a relatively large concentration of nitrogen compounds are found in plants. However, there is no direct evidence that any of this nitrogen is emitted into the atmosphere as NO_x. In contrast during decomposition NO_x can be emitted into the atmosphere but its significance is not known. During the ensiling process high concentrations of nitrogen oxides can be emitted. In an unventilated silo or enclosure, NO and NO_2 can reach hazardous levels and such levels have accounted for several fatalities (Commins, et al., 1971; Scaletti, et al., 1960). In decomposition of plant products only a small fraction of total nitrogen losses from the system are attributed to denitrification. In an eastern mature hardwood forest, an

estimated 3.6% of the total nitrogen flux was lost through denitrification processes (Mitchell, et al., 1975). Estimated denitrification rates of 0.17, 1.61 and 0.08 kg N ha^{-1} yr^{-1} were measured for branches, logs and litter (H layer), respectively (Todd, et al., 1975). It is conceivable that under some conditions small amounts of nitrogen oxides are emitted during litter decomposition. However, data on the emission rates from decomposition are lacking.

ESTIMATES OF GLOBAL NO_x EMISSION

The source of NO_x in the atmosphere is both anthropogenic and biogenic. Estimates of anthropogenic emissions of NO_x on a global basis are in good agreement as shown in Table 2. But the biogenic emissions are varied and are much more difficult to identify, measure, or estimate.

The biological and chemical transformations of nitrogen compounds in the soil appear to be the major source of NO_x. The estimates of NO_x emission rates from soil (Table 1) range from 0.01 - 0.2 kg N $km^{-2}hr^{-1}$. This rate computed on a global scale gives an emission from 3 to 58 $\times$ 10^9 kg N yr^{-1} and compares closely to the estimated global NO_x emissions by Galbally (1975) and Söderlund and Svensson (1976).

The background concentrations of NO and NO_2 reported by Rasmussen, et al. (1975) is about 0.3 - 2.5 µg m^{-3} and 2 - 2.5 µg m^{-3}, respectively. Söderlund and Svensson (1976) reported background concentrations of NO_x to range from 0.5 - 7.5 µg m^3 (as NO_2) depending on geographical location. If it is assumed that background NO_x is in a steady state condition, then NO_x deposition must be balanced by NO_x emission. The total wet and dry deposition of NO_x for the terrestrial system was estimated at 32 to 83 $\times$ 10^9 kg N yr^{-1} and for the aquatic system at 11 to 33 $\times$ 10^9 kg N yr^{-1} (Söderlund and

Svensson, 1976). Peterson (1977) estimated that NO_x is removed by wet and dry deposition processes at about 0.04 kg N $km^{-2}hr^{-1}$. This value is similar to soil NO_x emission rates given in Table 1. Therefore, background concentrations of NO_x can be explained in large part by biogenic NO_x emissions.

Table 2. Estimates of Global NO_x Emission

Sources of NO_x (10^9 kg N yr^{-1})		References
Anthropogenic	Biogenic	
16	234	Robinson and Robbins, 1970
18	* 72	McConnell, 1973
15	20	Galbally, 1975
19	8-25	Söderlund and Svensson, 1976
	3-58	estimated from data in Table 1.

* natural sources estimated at 4 or more times the anthropogenic sources.

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